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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Pr cess for the preparation of catalyst microspheres

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PROCESS FOR THE PREPARATION OF CATALYST MICROSPHERES

The present invention relates to a process for the preparation of catalyst particles with a particle diameter in the range 20-2000 micron.

Within the specification, the term catalyst also encompasses catalyst additives.

For several catalytic applications, such as fluidized bed processes, small catalyst particles are required. Such particles are generally produced by spray-drying a mixture of the catalyst ingredients.

Spay-drying involves pumping a slurry containing the catalyst ingredients through a nozzle (a high-pressure nozzle or a rotating wheel with nozzle) into a chamber heated with hot air. During this process, high shear is placed on the slurry, thereby creating small droplets that quickly dry in the heated chamber.

Depending on the type of nozzle used, the particle size distribution of the resulting catalyst particles depends on either the nozzle pressure or the rotating speed of the wheel, but generally lies in the range 30-90 microns.

Unfortunately, only slurries with a low solids content (i.e. below about 45 wt% solids) and, consequently, a high liquid content can be spray-dried. Slurries with higher solids content either are too viscous to be pumped through the nozzle, or will not give suitable droplets upon spraying.

Due to this low solids limitation, large volumes of liquid are required, which have to be evaporated during the drying step. This is energy inefficient.

This problem is solved by the process according to the present invention, which involves the following steps:

a) agitating one or more dry catalyst component(s),

b) spraying a liquid agent on the catalyst component(s) while continuing the agitation, and

c) isolating particles with the desired particle diameter.

This process requires less liquid than spray-drying. Hence, less liquid has to be evoporated in the drying step, making this process more energy efficient that spray-drying.

Suitable agitation techniqu s involve fluidization and high-shear mixing.

Fluidization is performed by fluidizing the catalyst component(s) in a steam of gas, generally air. A nozzle is present above the so-formed fluidized bed. Through this nozzle, the liquid agent is sprayed on the catalyst component(s). A suitable apparatus for performing this process is a fluidized bed granulator.

The gas velocity influences the size of the particles obtained. This gas velocity preferably ranges from 1-10 times the minimum fluidization velocity and most preferably from 1-5 times the minimum fluidization velocity, whereby the minimum fluidization velocity is defined as the minimum gas velocity required for upholding the catalyst component particles. It will be clear that this minimum velocity depends on the particle size: the larger the particles, the higher the required minimum gas velocity. Catalyst components for the preparation of FCC catalyst particles generally have a particle size up to about 10 microns.

The temperature of the gas preferably ranges from 20° to 700°C, more preferably from 50° to 200°C, and most preferably from 80°-120°C.

High-shear mixing is performed in a high-shear mixer. A nozzle is present in the mixer, above the catalyst component(s). Through this nozzle, the liquid agent is sprayed on the catalyst component(s)

The preferred shear ranges from 250 to 5000 s^{-1}, more preferably from 250 to 2500 s^{-1}, and most preferably from 500 to 1000 s^{-1}.

The temperature during high shear mixing is preferably below 100°C, more preferably below 50°C, and most preferably ambient.

Catalyst components which can be used in the process according to the invention include solid acids, silica, alumina, iron (hydr)oxide, (meta)kaolin, bentonite, anionic clays, saponite, sepiolite, smectite, montmorillonite, and mixtures thereof.

Suitable solid acids include zeolites such as zeolite beta, MCM-22, MCM-36, mordenite, faujasite zeolites like X-zeolites and Y-zeolites (including H-Y-zeolites, RE-Y zeolites, and USY-zeolites), pentasil-type zeolites like ZSM-5, non-zeolitic solid acids such as silica-alumina, sulphated oxides such as sulphated oxides of zirconium, titanium, or tin, sulphated mixed oxides of zirconium, molybdenum, tungsten, etc., and chlorinated aluminium oxides.

Suitable aluminas include boehmite, pseudoboehmite, transition aluminas like alpha-, delta-, gamma-, eta-, theta-, and chi-alumina, aluminium trihydrate such as gibbsite or bauxite ore concentrate (BOC), and flash-calcined aluminium trihydrate.
Examples of suitable anionic clays (also called hydrotalcite-like materials or layered double hydroxides) are Mg-Al anionic clays, Fe-Al anionic clays, Zn-Al anionic clays, Fe-Fe anionic clays, etc.

The catalyst components used have to be dry before starting the process according to the invention. The term 'dry' in this context means that not more than 90% of the pore volume of these components is filled with water.

Zeolites are usually prepared via crystallisation, washing/dewatering, ion-exchange with NH_4 and rare earth metals (RE), drying, calcination, and milling.
Most of the aluminas used for FCC applications are made via precipitation processes. These processes usually involve the sequential steps of precipitation, crystallisation, and dewatering. A suitable dewatering technique to obtain alumina sufficiently dry to be used in the process according to the invention uses a high-pressure filter.

Suitable liquid agents include water, acidic aqueous solutions, or aqueous silicon- and/or aluminium-containing solutions or suspensions. The term 'liquid agent' refers to liquid substances, e.g. liquids, solutions, or suspentions, that assist in binding of the particles. The liquid agent can initiate this binding either during step b), or later, for instance during an additional calcination step. Whether or not binding takes place during step b) depends on the liquid agent and the catalyst component(s) used.

The desired liquid agent depends on the desired binder.
In case anionic clay is the desired binder, water can be used as the liquid agent. Logically, in this case anionic clay is (one of) the catalyst component(s).
In case alumina is the desired binder, an acidic aqueous solution can be used as liquid agent, while a peptizable alumina such as pseudoboehmite is (one of) the catalyst component(s). On the other hand, aluminium chlorohydrol or aluminium nitrohydrol-containing suspensions can be used as liquid agent, irrespective of the type of catalyst component(s) used. Another option is to use water as the liquid agent while flash-calcined aluminium trihydrate is (one of) the catalyst component(s). Although the latter

combination does not result in binding of the particles during step b), it does so during an additional calcination step.

If silica is the desired binder, a solution or suspension containing a silicon compound is used as liquid agent, irrespective of the type of catalyst component(s) used. Examples of suitable silicon compounds are silica sol, sodium (meta) silicate, and precipitated silica.

More than one liquid agent can be used, which can be sprayed on the catalyst components sequentially. For instance, a silicon-containing solution or sol, or an aluminium chlorohydrol or nitrohydrol-containing sol can used as a first liquid agent, while an acidic solution can be used as a second liquid agent.

It is preferred to spray some water on the catalyst component(s) before spraying the liquid agent. The required amount of water being such that about 90% of the pores of the catalyst component(s) can be filled with water.

The liquid agent is preferably sprayed on the catalyst component(s) at a rate of 1-1.5 times the required amount divided by the residence time. This residence time generally ranges from about 1 to 30 minutes.

The droplet size is preferably between 1 and 20 μm.

Agitation is continued until the right particle size is obtained. In case of fluidized bed granulation, the gas velocity is selected in such a way that it can only uphold particles smaller than the desired size. Hence, once the particles have the desired size, they fall down.

The particles obtained by the process according to the invention range in size from about 20 to about 2000 microns, preferably 20-600 microns, more preferably 20-200 microns and most preferably 30-100 microns. For fluid catalytic cracking (FCC) applications a particle size between 30 and 100 microns is preferred.

If desired, the resulting particles are dried and/or calcined. In case the applied liquid agent does not result in binding during agitation step b), a calcination step might be required to initiate this binding.

Drying involves heating of the formed particles at a temperature preferably in the range 100-200°C. Calcination is preferably conducted at 300°-1200°C, preferably 300° - 800°C, and most preferably 300°-600°C for 15 minutes to 24 hours, preferably 1-12 hours and most preferably 2-6 hours.

The particles obtained by the process according to the invention can be used for various purposes, e.g. as a catalyst, adsorbent, etc. Suitable catalytic applications include Gas to Liquid processes (e.g. Fischer-Tropsch), E-bed and H-oil processes, reforming, isomerisation, alkylation, and auto exhaust catalysis.

EXAMPLES

Example 1

This Example describes the preparation of FCC catalyst particles with the following composition (on dry base): 15% alumina, 20% USY, 4% silicasol, 61% kaolin.

A fluidized bed granulator was filled with about 200 gram of a mixture of dry alumina, kaolin, and zeolite. The mixture is fluidized and afterwards 35 g of silicasol is sprayed on top of the fluidized bed with a rate of 4.8 g/min. Simultaneously, the inlet temperature of the gas is set on 70°C. Next, 10% nitric acid solution was sprayed on top of the fluidized bed through the same nozzle with a rate of 4.8 g/min. After addition of 100 gram of the nitric acid solution, liquid addition was stopped and the gas inlet temperature was set on 135°C to dry the material.
The resulting FCC particles have a mean diameter (d50) of 76 micron. SEM analysis showed that the particles had a uniform element distribution.

Example 2

This Example describes the preparation of FCC catalyst particles with the following composition (on dry base): 15% alumina, 20% USY, 10% ACH, 55% kaolin.
A fluidized bed granulator was filled with about 200 gram of a mixture of dry alumina, kaolin and zeolite. The mixture was fluidized and afterwards 90 gram of an aluminium chlorohydol suspension was sprayed on top of the fluidized bed with a rate of 4.8 g/min. Simultaneously, the inlet temperature of the gas is set on 70°C. Next, a 10% nitric acid solution was sprayed on top of the fluidized bed through th same nozzle

with a rate of 4.8 g/min. After addition of 100 gram of the nitric acid solution, the liquid addition is stopped and the gas inlet temperature was set on 135°C to dry the material. The resulting FCC particles had a mean diameter (d50) of 78 micron. SEM analysis showed that the particles had a uniform element distribution.

CLAIMS

1. Process for the preparation of catalyst particles with a particle diameter in the range 20-2000 micron, which process comprises the steps of:
   a) agitating one or more dry catalyst component(s),
   b) spraying a liquid agent on the catalyst component(s) while continuing the agitation, and
   c) isolating particles with the desired particle diameter.

2. Process according to claim 1 wherein agitation is performed by high-shear mixing.

3. Process according to claim 1 wherein agitation is performed by fluidization.

4. Process according to any of the preceding claims wherein at least one of the catalyst components is alumina, clay, or zeolite.

5. Process according to claim 4 wherein the catalyst particles are FCC catalyst particles or FCC catalyst additive particles.

6. Process according to any of the preceding claims wherein the liquid agent is selected from the group consisting of water, an aqueous acidic solution, a silicon-containing solution or suspension, a suspension comprising aluminium chlorohydrol and/or aluminium nitrohydrol, and mixtures thereof.

7. Process according to claim 2 wherein the shear applied on the catalyst component(s) during high-shear mixing ranges from 250 to 1000 s^{-1}.

ABSTRACT

The present invention relates to a process for the preparation of catalyst particles with a particle diameter in the range 20-2000 micron involving the steps of agitating one or more dry catalyst component(s), spraying a liquid agent on the catalyst component(s) while continuing the agitation, and isolating particles with the desired particle diameter. In contrast to the conventional way of preparing such particles, spray-drying, the present process allows the formation of small particles out of slurries with a high solids content. Hence, smaller amounts of liquid have to be evaporated, which makes the process energy efficient.